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Synthesis and Self-Assembly of Films Containing FeCoPt Nanoparticles

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ABSTRACT

$Fe_{49}Co_7Pt_{44}$ and $Fe_{40}Co_{17}Pt_{43}$ nanoparticles were synthesized by simultaneous chemical reduction of platinum acetylacetonate and cobalt acetylacetonate and thermal decomposition of iron pentacarbonyl. As-prepared the particles had a disordered face-centered cubic lattice with an average diameter of 3.2 nm and were superparamagnetic. These particles were well dispersed in a 50/50 mixture of hexane and octane. The particles self-assembled into ordered superlattices when deposited onto carbon coated Cu TEM grids or onto single crystal Si (100) substrates. After vacuum annealing (from 500°C to 700 °C), the particles transformed to the tetragonal phase. The coercivity of the film strongly depended on the composition and annealing temperature. For the $Fe_{49}Co_7Pt_{44}$ film, coercivity of 8700 Oe and a squareness of 0.75 after annealing at 700 °C for 30 minutes. XPS shows existance of oxidized iron and cobalt on the surface of film.

INTRODUCTION

Ordered superlattices of nanosize particles have received considerable attention in recent years, as they present an interest both for fundamental and potential applications. Some of methods used for preparing ordered superlattices from the liquid phase are Langmuir-Blodgett technique, [1] self-assembly by slowing evaporation of solvent [2-5], and electrophoretic deposition [6]. It has been found that formation of ordered closed-packing nanoparticle array requires the monodispersed particles and proper stabilization by surfactants. The synthesis of nanoparticles, characterized by a low size distribution, is a new challenge in solid-state chemistry. Due to their small size, nanoparticles exhibit novel material properties that differ considerably from those of the bulk solid state. Up to date, ordered self-assembly of nanocrystals has been successfully fabricated for several materials, such as Ag [2], Au [3], Fe_2O_3 [4], CoO [5].

Equatomic FePt and CoPt nanocrystals attracted high interest for the ultrahigh density magnetic hard media because they have large uniaxial magnetocrystalline anisotropies (K_u) due to their tetragonal $L1_0$ crystal structure. Recently, $(Co_{100-x}Fe_x)_{50}Pt_{50}$ thin films, with $20<x<68$, were reported to have K_u between FePt and CoPt [7]. Progress in magnetic recording density is due in part to the development of media with finer and finer grain magnetic films. It has been estimated that, if an magnetic nanocrystals with sizes down to ~3 nm, the storage density can be up to 100-1000 Gbits/in^2 [8-9]. Thin granular films of ferromagnetic materials formed by sputter deposition are already the basis of conventional rigid magnetic storage media. Recently, two chemical methods have been employed to produce magnetic cobalt nanoparticles, including

solution phase metal salt reduction in reverse micelles [10] and in organic solvent [11]. Ordered arrays of nanocrystal FePt alloy from simultaneous polyol reduction of $Pt(acac)_2$ and thermal decomposition of $Fe(CO)_5$ has also been reported [12]. However, we found any reports of the chemical synthesis and self-assembly of CoFePt nanoparticles.

EXPERIMENTAL DETAIL

Materials and synthesis

All materials were used without further purification. Iron pentacarbonyl [$Fe(CO)_5$], cobalt acetylacetonate [$Co(acac)_2$], platinum acetylacetonate [$Pt(acac)_2$], 1, 2-hexadecanediol, octyl ether, oleic acid and oleyl amine were purchased from Aldrich. Hexane and octane were from Fisher Scientific.

FeCoPt nanoparticles were prepared by simultaneous thermal decomposition of $Fe(CO)_5$ (1.0 mmol) and polyol reduction of $Co(acac)_2$ (from 0.1 to 0.25 M) and $Pt(acac)_2$ (0.5M) in organic solvent of octyl ether. $Pt(acac)_2$ and $Co(acac)_2$ were combined with 10 mL of dioctylether in a three-neck flask and dissolved at 120 °C under N_2 protection. 1,2-Hexandecanediol (390 mg) was dissolved in 10 mL of dioctylether and heated to 80°C. The dissolved 1,2-hexadecanediol, 0.13 mL of $Fe(CO)_5$, 0.16 mL of oleic acid and 0.17 mL of oleylamine were added to the above mixture of $Co(acac)_2$ and $Pt(acac)_2$ solution, respectively. Under nitrogen gas protection, the mixture solution was heated to 286°C (the boiling temperature of dioctylther). After being refluxed for 30 minutes, the reaction mixture was cooled down to room temperature. Ethanol (40 mL) was added to precipitate the particles. The particles were washed twice with ethanol to remove the excess diol and reaction byproducts, finally separated by centrifugation. The black products were purified by re-dispersing in hexane and re-precipitating by adding ethanol.

The FeCoPt particles were dispersed in 10 mL of mixture of (1:1) hexane and octane, containing 0.05mL of oleic acid and 0.05 mL of oleylamine. In order to obtain TEM image of self-assembled nanoparticles, The above surfactants stabilized FeCoPt dispersion was diluted four times with the mixture of (1:1) hexane and octane, and 0.01-0.05 mL of diluted dispersion were dropped on carbon-coated Cu TEM grids which were put on 0.3*0.3 mm^2 Si(100) waver in order to constrain the dispersion in the desired region. Samples assembled and annealed on SiO_2/Si(100) waver were also prepared for EDS, XPS, X-ray diffraction, and magnetic measurements. The as-deposited samples were annealed under vacuum (<1*10^{-7} torr) at 500 °C, 600 °C and 700 °C, respectively, for 30 minutes.

Characterization.

X-ray diffraction (XRD) data were acquired on Rigaku D/MAX-2BX Horizontal XRD Thin Film Diffractometer. Transmission electron microscopy (TEM) microphotographs were carried out on a Hitachi 8000 electron microscope operating at 200 kV. Energy Disperse spectroscopy (EDS) was obtained with a Philips XL 30 scanning electron microscope equipped with EDS. Chemical analysis was carried out with Kratos Axis 165 XPS/Auger system. Magnetic measurement was obtained with Princeton Micromag™ 2900 Alternating Gradient Magnetometor (AGM).

RESULTS AND DISCUSSION

Chemical and phase analysis of CoFePt nanopartices

The chemical composition of FeCoPt nanoparticles from EDS, table I, shows that the composition of the particles can be controlled by the relative amounts of Fe, Co and Pt charged to the reactor. The relationship is not direct as the amount of iron incorporated into the particles was less then the amount of iron pentacarbonyl charged to the reactor.

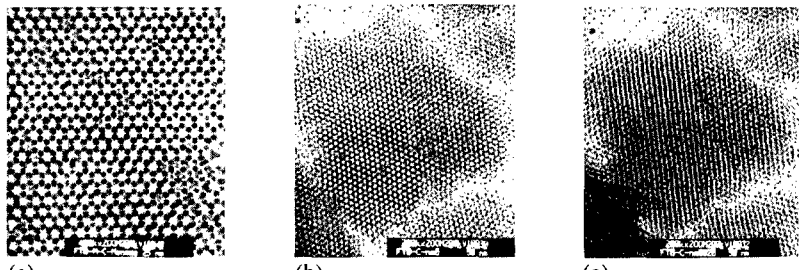
Table I. Comparison of the mole percent reactants charged to the reactor and the composition of the FeCoPt nanoparticles

Batch		Fe	Co	Pt
1	Charged	63	6	31
	Found	49	7	44
2	Charged	57	14	29
	Found	40	17	43

As-prepared the FeCoPt particles had a face center cubic lattice. The crystallite size was estimated to be 3.2 nm by analyizing the (111) peak from XRD. This number was close to the particle size of FeCoPt (3.6 nm) from TEM image. When the samples were annealed under vacuum or Ar mixed with 2% of hydrogen gas, the particles transformed to the tetragonal phase. The degree of transformation increased with annealing temperature from 500°C to 700°C. However, the samples were also sintered significantly when annealing temperature is above 600°C. After annealing at 600°C the crystallite size ($d_{crys(111)}$) of $Fe_{49}Co_7Pt_{44}$ increases to 6.0 nm and increased to 16.2 nm after annealing at 700°C.

Ordered self-assembly of as-prepared FeCoPt nanoparticles

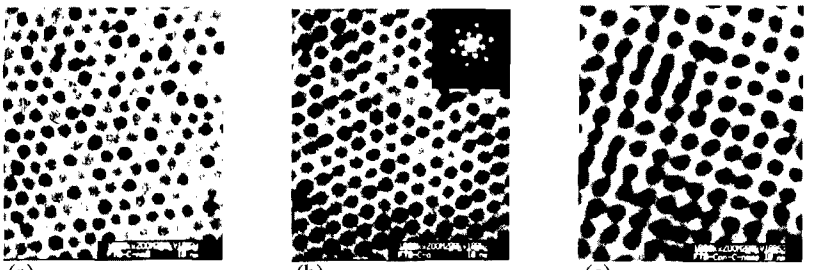
Fig.1 (a) show the 'honeycomb' arrays of $Fe_{49}Co_7Pt_{44}$ nanoparticles on the carbon-coated TEM grids. The ordered domain can extend to 150 nm in diameter. Sometimes, we also found wire arrays on the carbon-coated Cu grids. The 'honeycomb' and wire arrays actually both come from the hexagonal close-packing (HCP, ABAB stacking) of $Fe_{49}Co_7Pt_{44}$ nanoparticles. Fig. 1b and 1c show that "honeycomb" arrays can be transformed into "wire" array for HCP structure when tilting the sample by 20°.



(a) (b) (c)

Figure 1. 'Honeycomb' ordered superlattice of $Fe_{49}Co_7Pt_{44}$ nanoparticles as-deposited on carbon-coated Cu grid. (a) magnification of 400 k, (b) magnification of 200 k when sample is not tilted and (c) when sample was tilted by 20°.

When the film thickness increases, $Fe_{49}Co_7Pt_{44}$ nanoparticles tend to self-assemble from ABAB close-stacking to ABCABC close-packing. We usually observed a mixture of ABAB and ABCABC packing (Fig. 2a) and hexagonal arrays (Fig. 2b). The calculation from the small angle electron diffraction pattern show the interparticle distance is 6.67 nm, which is about the twice of particle size.



(a) (b) (c)

Figure 2. Ordered superlattices of CoFePt nanoparticles superlattices as-deposited on carbon-coated Cu grid. (a) & (b) Hexagonal, and (c) square nanoparticle lattice. The insert in (b) is small angle electron diffraction pattern of the sample.

Sometimes we also find square arrays for the thicker film (Fig.2c). The square arrays (more exactly, FCC particle latice) can be viewed as ABCABC close-packing of nanoparticles from [111] direction. The average interparticle distance in Fig3a and 3b is about 6.67 nm, which is 1.42 times of that in Fig. 2c (4.69 nm). This confirmed that the hexagonal and square arrays are from the same kind of stacking, but from different view direction.

Magnetic properties of FeCoPt films

Magnetic hysteresis curves were measured on an alternating gradient magnetometer. As-prepared the self-assembled FeCoPt films were superparamagnetic. After annealing under vacuum (10^{-7} torr) or Ar with 2% of H_2 gas, the films became ferromagnetic. Table II shows that the coercivity of FeCoPt film increases with annealing temperature. As the atomic percentage of cobalt increased, the coercivity decreased.

Table II. Coercivity (Oe) of self-assembled FeCoPt films (fixed annealing time for 30 minutes).

Annealing Temperature	500°C	600°C	700°C
$Fe_{48}Pt_{52}$	3970	6500	< 11600*
$Fe_{49}Co_7Pt_{44}$	2430	4500	8700
$Fe_{40}Co_{17}Pt_{43}$		3800	6590

* minor loop

CONCLUSIONS

We prepared $Fe_{49}Co_7Pt_{44}$ and $Fe_{32}Co_{21}Pt_{46}$ nanoparticles by simultaneous chemical reduction of platinum acetylacetonate and cobalt acetylacetonate and thermal decomposition of iron pentacarbonyl. As-prepared particles had an average diameter of 3.2 nm and were superparamagnetic. These nanoparticles were well dispersed in a hexanone or octane. FeCoPt tended to self-assemble into ordered arrays with either ABAB close-packing for the thin films or ABCABC close-packing for thick films while deposited onto a silica coated Cu TEM grids. The coercivity of FeCoPt film increased with annealing temperature, but decreased as the atomic percentage of cobalt increased.

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